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(54) ELECTROLUMINESCENT DEVICES WITH ELECTRODE PROTECTION

ELEKTROLUMINESZIERENDE ANORDNUNGEN MIT ELEKTRODENSCHUTZ

DISPOSITIFS ELECTROLUMINESCENTS AVEC PROTECTION D'ELECTRODE

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(56) References cited:
US-A- 5 247 190 **US-A- 5 558 904**

- **DATABASE WPI Section Ch, Week 9343 Derwent Publications Ltd., London, GB; Class A26, AN 93-339976 XP002040832 & JP 05 247 460 A (SUMITOMO CHEM CO LTD), 24 September 1993**
- **DATABASE WPI Section EI, Week 9717 Derwent Publications Ltd., London, GB; Class U14, AN 97-185344 XP002040833 & JP 09 045 479 A (HEWLETT-PACKARD CO), 14 February 1997**

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DescriptionField of the Invention

5 **[0001]** This invention relates to the construction of organic electroluminescent (EL) devices.

Background of the Invention

10 **[0002]** Organic electroluminescent devices are made from materials that emit light when a suitable voltage is applied across electrodes deposited on either side of the material. One class of such materials is semiconductive conjugated polymers which have been described in our earlier Patent US 5,247,190, the contents of which are herein incorporated by reference. Poly(p-phenylene vinylene) [PPV], for instance, will emit light when positive and negative charge carriers are passed through the material by applying a voltage between two suitable electrodes. The electroluminescent efficiency of these devices depends on the balancing of the electrons and holes that are injected into the device and meet to form electron/hole pairs, as well as on the efficiency with which these electron/hole pairs combine to radiate light, i. e. the photoluminescence efficiency (for example, see N.C. Greenham and R.H. Friend, Solid State Physics, 49, 1, 1995). Therefore it is of importance for an efficient device to have sufficiently high photoluminescence efficiency.

15 **[0003]** There are several approaches used for the processing of conjugated polymers. One approach uses a precursor polymer which is soluble and can therefore be easily coated by standard solution-based processing techniques (for example, spin-coating and blade-coating). The precursor is then converted in situ by suitable heat treatment to give the conjugated and insoluble polymer. Another approach uses directly soluble conjugated polymers which do not require a subsequent conversion stage. Depending on the specific application, one or other of the approaches might be relevant. The precursor polymers approach can be especially important where subsequent processing might lead to damage of the polymer film if it were directly soluble - such processing may be, for instance, coating with further polymer layers (for example, transport layers or emitting layers of different colour), or patterning of the top electrode. Converted precursor films also have better thermal stability which is of importance both during fabrication but also for the storage and operation of devices at high temperatures.

20 **[0004]** Where the precursor polymer is converted to the final form by elimination or modification of a solubilising group it is generally important that these by-products of the conversion process are removed from the film. It may also be important that they do not interact with the substrate during this process, for example if this causes harmful impurities to move into the film from the substrate thus affecting the performance (including luminescence efficiency and lifetime) of the electroluminescent device. We have observed, for instance, a quenching of the photoluminescence when precursor PPV polymers are converted on conductive oxide substrates such as indium tin oxide. This, we believe, may be caused by indium compounds being released into the PPV due to the reaction of one of the conversion by-products (for example, hydrogen halide) with the indium tin oxide.

25 **[0005]** In addition to the observation of quenching via the presence of impurities from the interaction of by-products with indium tin oxide during conversion, we have also observed detrimental effects due to the enhanced conversion of certain PPV copolymers. Such copolymers normally have limited conjugation lengths as compared to the homopolymer case. This normally leads to exciton confinement and therefore high photoluminescence and electroluminescence efficiencies. In this case, we believe that the indium compounds present in certain PPV copolymers films when converted on indium tin oxide can catalyse the elimination of groups designed to survive the conversion process.

Summary of the Invention

30 **[0006]** According to one aspect of the invention there is provided a method of manufacturing an electroluminescent device comprising the steps of:

forming an anode of a positive charge carrier injecting material;

forming an anode protection layer on the anode of a protection material selected from the group comprising:

50 polypyrroles and their derivatives; polythiophenes and their derivatives; polyvinylcarbazole (PVK); polystyrene; poly(vinyl pyridine); dielectric materials; carbon; amorphous silicon; non-indium containing conductive oxides including tin oxide, zinc oxide, vanadium oxide, molybdenum oxide and nickel oxide; and sublimed organic semiconductors;

55 forming a light emissive layer by converting a precursor to a polymer being a semiconductive conjugated polymer; and

forming a cathode of a negative charge carrier injecting material.

[0007] The anode protection layer has been found to be particularly valuable when the light emissive layer is a polymer which releases acidic by products (e.g. hydrogen halides) during the conversion from the precursor to the conjugated polymer.

[0008] Another aspect of the invention provides an electroluminescent device comprising:

- an anode formed of a positive charge carrier injecting material;
- an anode protection layer on the anode formed of a protection material selected from the group comprising: polypyrroles and their derivatives;
- polyvinylcarbazole (PVK); polystyrene; poly(vinyl pyridine); dielectric materials; carbon; amorphous silicon;
- non-indium containing conductive oxides including tin oxide, zinc oxide, vanadium oxide, molybdenum oxide, and nickel oxide; and sublimed organic semiconductors;
- a light emissive layer formed of a semiconductive conjugated polymer; and
- a cathode formed of a negative charge carrier injecting material.

[0009] The invention is particularly useful when the anode is formed of indium tin oxide (ITO). However other materials are suitable, such as tin oxide.

[0010] In one embodiment a layer of transparent conducting material deposited on glass or plastic forms the anode of the device. Examples of suitable anodes include tin oxide and indium tin oxide. Typical layer thicknesses are 500-2000Å and sheet resistances are 10-100 Ohm/square, and preferably <30 Ohm/square. The converted precursor polymer can be, for instance, poly(p-phenylene vinylene) [PPV] or a homopolymer or copolymer derivative of PPV. The thickness of this layer can be in the range 100-3000Å, preferably 500-2000Å and more preferably 1000-2000Å. The thickness of the precursor layer prior to conversion can be in the range 100-6000Å for spin-coated layers and up to 200µm for blade coating. The anode protection layer is chosen to act as a barrier against the conversion by-products of the precursor polymer, but also should not act as a barrier to the injection of holes from the anode into the emitting layer, where they combine with electrons injected from the cathode to radiate light. Conducting polymers are a general class of materials that can combine ease of processing, protection of the underlying electrode, and suitable hole transporting and injecting properties and are therefore good candidates. Thin layers of between 10-2000Å and preferably 10-500Å may be used and therefore the transparency of the layer can be high. Typical sheet resistances of these layers are 100-1000 Ohm/square, but can be as high as in excess of 10¹⁰ Ω/squ. Examples include conjugated polymers that have been doped including polythiophenes, polyanilines, polypyrroles, and derivatives thereof. The cathode electrode is placed on the other side of the converted precursor material and completes the device structure. Furthermore, undoped conjugated polymers, as listed above, may also be used where the doping occurs in situ, by interaction with the conversion by-products during device manufacture.

[0011] The invention also provides use of an electrode protection layer in the manufacture of an organic light emitting device to protect an electrode of the organic light emitting device from the effects of conversion of a precursor into a light emitting semiconductive conjugated polymer, wherein the organic light emitting device comprises first and second electrodes with the light emitting polymer being located between them.

[0012] Thus, in another embodiment the electrode protection layer and the precursor polymer is deposited on the cathode, typically a material such as aluminium or an alloy of aluminium with a low work function element or any low work function element or alloy. In this case the protection layer will need to transport electrons, but may or may not need to be transparent. Again conducting polymers are suitable candidates as cathode protection layers. The anode electrode is placed on the other side of the converted precursor material and completes the device structure.

[0013] In yet another embodiment a protection layer to either the anode or cathode as described above is provided but where the protection layer is an undoped conjugated polymer but which has sufficient injection properties and transport mobilities for either holes or electrons depending on whether it is protecting the anode or cathode respectively. An example of such a protection layer would be a soluble PPV derivative or alternatively a precursor PPV or PPV derivative material. In the latter case, if the protection layer is much thinner than the electroluminescence layer, the by-products of the conversion process are more easily removed and therefore any interaction with the electrode during conversion is reduced.

[0014] In yet another embodiment a protection layer to either the anode or cathode as described above is provided, but where the protection layer is an evaporated, sputtered, or reactively sputtered thin film which has sufficient injection properties and transport mobilities for either holes or electrons depending on whether it is protecting the anode or cathode respectively. An example of such a protection layer would be a thin layer of sputtered or evaporated carbon, a sputtered layer of amorphous silicon or non-indium containing conductive oxides including tin oxide, zinc oxide, vanadium oxide, molybdenum oxide, and nickel oxide, or a sublimed organic semiconductor layer.

[0015] In yet another embodiment a protection layer to either the cathode or anode as described above is provided, but where the protection layer is an undoped and non-conjugated polymer but which has sufficient injection properties and transport mobilities for either holes or electrons depending on whether it is protecting the anode or cathode re-

spectively. An example would be polyvinyl carbazole which is a good hole transporting material but is not a conjugated polymer. Alternatively very thin layers of polymer materials which have relatively poor hole and electron mobilities may function as good electrode protectors without compromising the balance of electron and hole charge carriers. Examples would be polystyrene and poly(vinyl pyridine).

[0016] In yet another embodiment a protection layer to either the cathode or anode as described above is provided, but where the protection layer is a very thin inorganic dielectric which provides a barrier to the precursor conversion by-products, but which is thin enough that holes can tunnel through it when it is in contact and protecting the anode or electrons can tunnel through it when it is in contact and protecting the cathode.

[0017] The invention also provides a method of manufacturing an electroluminescent device comprising the steps of:

- forming an anode of a positive charge injecting material;
- forming a sacrificial anode protection layer over the anode;
- depositing a precursor to a semiconductive conjugated polymer on the sacrificial layer;
- converting the precursor to a semiconductive conjugated polymer to form a light emitting layer, during which conversion step the anode protection layer protects the anode from the effects of the conversion and is itself consumed;
- and
- forming a cathode of a negative charge injecting material.

[0018] Thus, in another embodiment a protection layer for either the anode or the cathode as described above is provided, but where the protection layer is a sacrificial layer. During the conversion process the sacrificial layer is etched away by the conversion by-products, the subsequent products of this interaction are chosen such that they do not interfere with the photoluminescence or electroluminescence efficiencies of the converted precursor conjugated polymers. Examples of such protection layers would include non-stoichiometric oxide films, such as silicon and aluminium oxides, the layer thickness being determined by the degree of interaction during the conversion process.

[0019] The invention also provides the use in an electroluminescent device comprising an anode formed of a positive charge carrier injecting material a cathode formed of a negative charge carrier injecting material and a light emissive layer formed of a semiconductive conjugated polymer located between the anode and the cathode of a protection layer located between the light-emissive layer and the anode and formed of a protection material selected from the group comprising: polypyrroles and their derivatives; polythiophenes and their derivatives; polyvinylcarbazole (PVK); polystyrene; poly(vinylpyridine); dielectric materials; carbon; amorphous silicon; non-indium containing conductive oxides including tin oxide, zinc oxide vanadium oxide, molybdenum oxide and nickel oxide for protecting the light-emissive layer from the anode.

[0020] The invention also provides an electroluminescent device comprising an anode formed of a positive charge carrier injecting material; a layer of polyethylene dioxythiophene (PEDT) polystyrene sulphonate (PSS) on the anode, the molar ratio of PSS to PEDT being greater than 1.2:1; a light emissive layer formed of a semiconductive conjugated polymer; and a cathode formed of a negative charge carrier injecting material.

Brief Description of the Drawings

[0021]

- Figures 1A to 1C are diagrams of an electroluminescent device incorporating an anode protection layer;
- Figure 2 illustrates two conversion routes of a precursor to PPV;
- Figure 3A and 3B are graphs illustrating the UV - vis spectra of PPV homopolymer respectively converted on quartz, indium tin oxide and an anode protection layer;
- Figure 4 is a graph illustrating the UV - vis spectra of PPV copolymer converted on quartz, indium tin oxide and an anode protection layer; and
- Figure 5 is a diagram illustrating the IR spectra of an acetate based copolymer converted on silicon, silicon with an indium layer, and silicon with an indium layer and protection layer.

[0022] For a better understanding of the present invention and to show how the same may be carried into effect reference will now be made by way of example to the above referenced drawings.

Description of the Preferred Embodiments

[0023] Figure 1A illustrates a structure of an electroluminescent device. A substrate 2 formed of a transparent glass or plastics material is coated with a material constituting an anode 4 of the device. An anode protection layer 6 is located between the anode 4 and a light emitting layer 8. Cathode strips 10 are provided delineating with the anode 4

light emitting areas of the device. The operation of this device to emit light (without the anode protection layer) is discussed in our preceding referenced Patent US 5,247,190 and will not be described further herein except to the extent that it is affected by the present invention.

Embodiment I

[0024] A first embodiment is now described. Indium tin oxide constituting the anode 4 is deposited using either dc or rf sputtering techniques onto the polished glass substrate 2. Such substrates are available commercially. Soda lime glass with a thin silica barrier and an indium tin oxide layer of resistivity of 30 Ohm/square and transparency of about 85%, with a thickness of order 1500Å, can be used. A polythiophene based conducting polymer system is used as the anode protection layer 6. Polyethylene dioxythiophene/polystyrene sulphonate (PEDT/PSS @ 1:1.2 molar ratio) - which is available from Bayer AG, Leverkusen, Germany as Trial Product AI 4071. A 100Å film of the conducting polymer is spin-coated on the substrate. The EL layer 8 is formed by spin-coating a precursor polymer such as a homopolymer PPV. With this precursor polymer the solubilising group that is removed during conversion at 150°C in nitrogen for 4 hours is tetrahydrothiophene, and the counter-ion to the thiophene salt is bromide. Another by-product is therefore hydrogen bromide which readily attacks ITO and can cause the release of detrimental products into the film which quenches the photoluminescence. The conversion by-products of the PPV-based precursor are indicated in Figure 2 where $a=0$, $a'=0$.

[0025] Without the anode protection layer, initial measurements of PL efficiency of the PPV material were reduced from about 13% to, at best, about 0.7% following the thermal conversion process.

Further measurements established that the PL efficiency may be in the range 10% down to about 2-3%. Initial measurements with the anode protection layer indicated a PL efficiency of ~3%. Subsequent work has shown that this can be increased to ~5%. After the conversion a suitable cathode material, calcium for instance, is deposited on top of the conjugated polymer 8 and patterned to form strips 10. After that, contacting and encapsulation with epoxy/glass were immediately performed in a glove box. Devices made with the protector layer typically have significantly improved electroluminescence efficiency compared to the devices without the protector layer 6.

Embodiment II

[0026] Another specific embodiment is now described. The initial steps are the same as embodiment I up to formation of the EL layer. In this embodiment, a precursor to an acetate-based PPV copolymer is deposited. This material has a very high photoluminescence (PL) efficiency, where the solubilising group that is removed during conversion is tetrahydrothiophene, and the counter-ion to the thiophene salt is bromide. Another by-product is therefore hydrogen bromide which readily attacks ITO and can cause the release of detrimental products into the film which quenches the photoluminescence and causes enhanced conversion. Without the anode protection layer 6, the PL efficiency of the PPV material is dramatically reduced from about 50-60% to, at best about 7% following the thermal conversion process (150°C in nitrogen for 4 hours as before). However, with the protector layer a PL efficiency of ~22% is obtained following conversion. Figure 2 shows the conversion system, where $a \neq 0$, $a' \neq 0$. After the conversion a suitable cathode material, calcium for instance, is deposited on top of the conjugated polymer.

[0027] Table 1 illustrates the photoluminescent efficiencies for embodiments I and II, in the final column of Table 1. The first and second columns of Table 1 illustrate values for the photoluminescence efficiency in situations where the precursor layer is spin-coated onto quartz and indium tin oxide respectively without the use of the anode protection layer. Table 1A shows equivalent figures resulting from what we believe are more accurate measurements with a better statistical base.

[0028] The copolymer referred to in this case was measured initially to contain ~20 mol.% of the acetate function. Subsequent measurements which we believe to be more accurate indicate a content of ~40 mol.% of the acetate function. Modification of the copolymer acetate level has led to photoluminescence efficiencies of about 30% when converted on ITO with the PEDT/PSS protection layer.

[0029] Figures 3 to 5 show that protection of the PPV copolymer is also brought about minimising the enhanced conversion with the ITO protection layer. Figure 3A illustrates measurements taken from structures having differing layer thicknesses. Figure 3B shows the situation where a common layer thickness is used. Figure 3B illustrates that the UV - vis spectra show little change in the homopolymer case irrespective of the substrate used. However, Figure 4 shows that there is an enhanced red shift for the acetate based copolymer when converted on ITO. In addition, there is an absorption peak at 1737 cm⁻¹ in the IR spectra which is assigned to the acetate carbonyl absorption. The relative intensity of this can be compared with other peaks in the spectrum, such as the absorption at 1517 cm⁻¹ which originates in the aromatic constituents of the polymer. The ratio of the intensities of the two peaks therefore gives a measure of the relative quantities of the acetate function. Table 2 shows that this ratio (acetate:aromatic) is significantly reduced when the conversion is carried out on silicon with an indium layer. We interpret these results as enhanced conversion

of the acetate based copolymer by indium compounds from the silicon substrate with indium layer and this process is reduced by the presence of protection layers. Relative photoluminescence efficiencies are detailed in Tables 1A and B. The device performance of the systems including the protection layer may be summarised as 100cd/m² starting brightness, efficiency of 0.2-0.6 lm/W and up to 2 lm/W, with a half-life of brightness (at constant current or constant voltage drive) of 10-100 hours, and up to 2000 hours.

Embodiment III

[0030] Another specific embodiment is now described. In this embodiment, the production steps are the same for Embodiment II except that the polyethylene dioxythiophene/polystyrene sulphonate material which is used as the anode protection layer has been optimised to give beneficial lifetime performance by increasing the PSS content. Thus, the material now has a 1:5 molar ratio PEDT/PSS. The device performance of these system may be summarised as 100 cd/m² starting brightness, efficiency of 0.3-1.2 lm/W, and up to 2 lm/W with a half-life of ~500 hours and up to 2000 hours.

Embodiment IV

[0031] In the case of Embodiment III, we have observed a detrimental interaction between the PEDT/PSS protection layer (@ 1:5 molar ratio) with the PPV precursor solution. We believe this is because of dissolution of the PEDT/PSS layer in the PPV precursor solution and this can lead to non-uniform emission in the final device. For example, if the PPV is spin-coated on top of the PEDT/PSS film during device fabrication then a circular nonuniformity is observed at the PEDT/PSS-PPV interface after conversion. We have overcome this problem by spin-coating a thin poly(vinyl pyridine) (PVP) film (Figure 1B - reference 7) on top of the PEDT/PSS layer before the PPV precursor solution is applied. As is well understood, commercially available PVP includes a component of polystyrene, typically 10%, to render it soluble. Hence, a 100Å film of the PEDT/PSS system is deposited as described above and following this a thin PVP film is spin-coated from a 0.1% w/v solution in methanol. The rest of the device is manufactured in the normal way and characteristics as outlined above are obtained (i.e. 100 cd/m² initial brightness, 0.3-1.2 lm/W efficiency, with a half-life of ~500 hours). However, the emission uniformity is greatly improved. As the PVP acts as a barrier between the PEDT/PSS system and the PPV, this approach can also be used to pattern this ITO protection layer.

Embodiment V

[0032] A further specific embodiment is now described and relates to the fabrication of such devices. A sheet of ITO coated glass is taken and cleaned. The dimensions of the ITO-coated glass may be from 12*12 mm to much greater than 80*80 mm. The PEDT/PSS ITO protection layer is then spin-coated onto the substrate to a thickness of ~100Å. Following this the PPV precursor solution is blade-coated onto the PEDT/PSS layer at a wet film thickness of 100 µm at a precursor solution concentration of 0.4-0.5% solid content. In this case the device uniformity is superior to that obtained when the PPV precursor is spin-coated. Alternatively, a double layer PPV device may be blade-coated such that each layer is ~500-700Å thick and a short conversion (~20 minutes at 150°C) is carried out before deposition of the second layer (reference 9 in Figure 1C). After conversion the final conversion the PPV film obtained is ~1000-1400Å thick. In this case beneficial effects are observed with respect to device efficiency and gross uniformity. A suitable cathode is then deposited and the device is connectorised.

Embodiment VI

[0033] In another embodiment, a glass substrate is coated with indium tin oxide in the manner described above. Then, PVP was dissolved in methanol to a concentration of 0.1%, prefiltered to 1 micron pore size and coated onto the indium tin oxide to a thickness of about 100Å. Then, the PPV precursor discussed above with reference to Embodiment I is spincoated on top and converted at 150°C in nitrogen for 4 hours to render a layer of PPV of about 1000Å thickness. The device was then stored in a desiccator for 48 hours before a cathode formed from an aluminium/lithium alloy was sputtered on top.

Embodiment VII

[0034] This embodiment was formed in the same manner as Embodiment VI, except that the anode protection layer was formed of polyvinylcarbazole (PVK) dissolved in THF to a concentration of 0.1%.

Embodiment VIII

[0035] This embodiment was formed in the same manner as Embodiments VI and VII except that the anode protection layer was formed of polystyrene dissolved in THF to a concentration of 0.1%.

Embodiment IX

[0036] This embodiment was formed in the same manner as Embodiments VI, VII and VIII except that the anode protection layer was formed of poly(vinyl pyridine) dissolved in methanol to a concentration of 0.1%.

Embodiment X

[0037] In another embodiment, the device is manufactured according to Embodiment II, but the cathode is formed of a lithium/aluminium alloy instead of calcium. For instance a lithium/aluminium alloy containing up to 10% by weight Li, is sputtered on top of the conjugated polymer to a thickness of 10Å-1µm and preferably ~1200Å. The Li/Al alloy targets are commercially available and can typically contain ~2.5% by weight Li. Other stabilising elements such as Zr, Mg, Cu may also be present. Devices made with the protector layer and the lithium based cathode have significantly improved electroluminescence efficiencies compared to the devices without the protector layer and using say calcium electrode.

[0038] Thus, the various embodiments described above of the present invention each provide a multilayer electroluminescent device incorporating a converted precursor polymer as the emitting layer and an electrode protecting layer placed between the converted precursor polymer and the underlying electrode and which acts to protect the electrode during the precursor conversion process. At least one other layer is present one of which is the second electrode.

[0039] The embodiments described above are illustrative of a method of manufacture of an electroluminescence device wherein a precursor to a conjugated polymer material is deposited on a substrate on which has previously been deposited both an electrode layer and subsequently an electrode protection layer. The precursor is then converted to the final conjugated polymer form before deposition of a subsequent layer or layers at least one of which is the second electrode.

TABLE 1

TYPICAL PHOTOLUMINESCENCE EFFICIENCY (%) MEASUREMENTS			
Polymer Type	PL eff/Quartz	PL eff/ITO	PL eff/Protection Layer /ITO
Homopolymer	13.2	0.7	3
Copolymer	56	6.8	22

TABLE 1A

IMPROVED PHOTOLUMINESCENCE EFFICIENCY (%) MEASUREMENTS			
Polymer Type	PL eff/Quartz	PL eff/ITO	PL eff/Protection Layer/ITO
Homopolymer	10	2-3	4-5
Copolymer	50-60	7	20

TABLE 2

1737/1517 cm ⁻¹ Ratios (Acetate:Carbonyl) from IR spectra	
Substrate	1737/1517 cm ⁻¹ Ratio*
Inert(Si)	1.1
Si with indium layer with protection	1
Si with indium layer	0.3

Claims

1. A method of manufacturing an electroluminescent device comprising the steps of:

5 forming an anode of a positive charge carrier injecting material;
forming an anode protection layer on the anode of a protection material selected from the group comprising:
polypyrroles and their derivatives; polythiophenes and their derivatives; polyvinylcarbazole (PVK); polystyrene;
poly(vinyl pyridine); dielectric materials; carbon; amorphous silicon; non-indium containing conductive oxides
10 including tin oxide, zinc oxide, vanadium oxide, molybdenum oxide and nickel oxide; and sublimed organic
semiconductors;
forming a light emissive layer by converting a precursor to a polymer being a semiconductive conjugated
polymer; and
forming a cathode of a negative charge carrier injecting material.

15 2. A method as claimed in claim 1, wherein the semiconductive conjugated polymer is selected from a class of polymers which release acidic by products during the conversion from the precursor polymer to the conjugated polymer.

20 3. A method as claimed in claim 1 or 2, wherein the anode comprises a transparent conducting layer deposited on a substrate of a glass or plastics material.

4. A method as claimed in claim 1 or 2, wherein the light emissive layer is formed from a homopolymer of poly(p-phenylene vinylene) (PPV).

25 5. A method as claimed in claim 1 or 2, wherein the light emissive layer is formed from an acetate based copolymer of PPV.

30 6. A method as claimed in any preceding claim, wherein the anode protection layer is formed from polyethylene dioxythiophene/polystyrene sulphonate.

7. A method as claimed in claim 6, wherein the molar ratio of the anode protection layer is 1:1.2 PEDT/PSS.

8. A method as claimed in claim 6, wherein the molar ratio of the anode protection layer is 1:5 PEDT/PSS.

35 9. A method as claimed in any preceding claim, wherein a further layer is deposited between the anode protection layer and the light emissive layer to improve coating uniformity of the light emissive layer.

10. A method as claimed in claim 9, wherein the further layer comprises poly(vinyl pyridine) (PVP).

40 11. A method as claimed in any preceding claim, wherein a second light emissive layer is provided between the anode protection layer and the cathode.

45 12. A method as claimed in any of claims 1 to 5, wherein when the anode protection layer is formed of carbon, tin oxide or silicon it is formed by sputtering or evaporating.

13. A method as claimed in any preceding claim, wherein the thickness of the anode protection layer is between 10 and 500Å.

50 14. A method according to any preceding claim, wherein the thickness of each of the anode and light emissive layer is between 500 and 2000Å.

15. A method according to any preceding claim, wherein the anode is formed of ITO.

55 16. A method according to any preceding claim, wherein the cathode is formed of aluminium or an aluminium alloy.

17. An electroluminescent device comprising:

an anode formed of a positive charge carrier injecting material;

an anode protection layer on the anode formed of a protection material selected from the group comprising: polypyrroles and their derivatives;

polyvinylcarbazole (PVK); polystyrene; poly(vinyl pyridine); dielectric materials; carbon; amorphous silicon; non-indium containing conductive oxides including tin oxide, zinc oxide, vanadium oxide, molybdenum oxide and nickel oxide;

a light emissive layer formed of a semiconductive conjugated polymer; and
a cathode formed of a negative charge carrier injecting material.

18. A device as claimed in claim 17, wherein the thickness of the anode protection layer is between 10 and 500Å.

19. A device according to claim 17 to 18, wherein the thickness of each of the anode and light emissive layer is between 500 and 2000Å.

20. A device according to any of claims 17 to 19, wherein the anode is formed of ITO.

21. A device according to any of claims 17 to 20, wherein the cathode is formed of aluminium or an aluminium alloy.

22. A method of manufacturing an electroluminescent device comprising the steps of:

forming an anode of a positive charge injecting material;
forming a sacrificial anode protection layer over the anode;
depositing a precursor to a semiconductive conjugated polymer on the sacrificial layer;
converting the precursor to a semiconductive conjugated polymer to form a light emitting layer, during which conversion step the anode protection layer protects the anode from the effects of the conversion and is itself consumed; and
forming a cathode of a negative charge injecting material.

23. Use of an electrode protection layer in the manufacture of an organic light emitting device to protect an electrode of the organic light emitting device from the effects of conversion of a precursor into a light emitting semiconductive conjugated polymer, wherein the organic light emitting device comprises first and second electrodes with the light emitting polymer being located between them.

24. Use in an electroluminescent device comprising:

an anode formed of a positive charge carrier injecting material a cathode formed of a negative charge carrier injecting material and a light emissive layer formed of a semiconductive conjugated polymer located between the anode and the cathode;
of a protection layer located between the light-emissive layer and the anode and formed of a protection material selected from the group comprising: polypyrroles and their derivatives; polythiophenes and their derivatives; polyvinylcarbazole (PVK); polystyrene; poly(vinylpyridine); dielectric materials; carbon; amorphous silicon; non-indium containing conductive oxides including tin oxide, zinc oxide vanadium oxide, molybdenum oxide and nickel oxide for protecting the light-emissive layer from the anode.

25. A use as claimed in claim 24, wherein the thickness of the protection layer is between 10 and 500Å.

26. A use according to claim 24 or 25, wherein the thickness of each of the anode and light emissive layer is between 500 and 2000Å.

27. A use according to any of claims 24 to 26, wherein the anode is formed of ITO.

28. A use according to any of claims 24 to 27, wherein the cathode is formed of aluminium or an aluminium alloy.

29. An electroluminescent device comprising:

an anode formed of a positive charge carrier injecting material;
a layer of polyethylene dioxythiophene (PEDT) polystyrene sulphonate (PSS) on the anode, the molar ratio of PSS to PEDT being greater than 1.2:1;
a light emissive layer formed of a semiconductive conjugated polymer; and

a cathode formed of a negative charge carrier injecting material.

30. A device according to claim 29 wherein the molar ratio of PSS to PEDT is 5:1 or greater.

5

Patentansprüche

1. Verfahren zur Herstellung eines Elektrolumineszenz-Bauelements, mit den folgenden Schritten:

10

Bilden einer Anode aus einem positive Ladungsträger injizierenden Material;

15

Bilden einer Anodenschutzschicht auf der Anode aus einem Schutzmaterial, das aus der folgenden Gruppe ausgewählt wird: Polypyrrole und ihre Derivate; Polythiophene und ihre Derivate; Polyvinylcarbazol (PVK); Polystyrol; Poly(vinylpyridin); dielektrische Materialien; Kohlenstoff; amorphes Silizium; kein Indium enthaltende leitfähige Oxide, einschließlich Zinnoxid, Zinkoxid, Vanadiumoxid, Molybdänoxid und Nickeloxid; und sublimierte organische Halbleiter;

20

Bilden einer lichtemittierenden Schicht durch Umwandeln eines Precursors in ein Polymer, das ein halbleitendes konjugiertes Polymer ist; und

Bilden einer Kathode aus einem negative Ladungsträger injizierendem Material.

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2. Verfahren nach Anspruch 1, wobei das halbleitende konjugierte Polymer aus einer Klasse von Polymeren, die während der Umwandlung des Precursor-Polymers in das konjugierte Polymer saure Nebenprodukte freigegeben, ausgewählt wird.

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3. Verfahren nach Anspruch 1 oder 2, wobei die Anode eine auf einem Substrat aus einem Glas- oder Kunststoffmaterial abgelagerte transparente leitende Schicht umfaßt.

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4. Verfahren nach Anspruch 1 oder 2, wobei die lichtemittierende Schicht aus einem Homopolymer von Poly(p-phenylenvinyle) (PPV) gebildet wird.

5. Verfahren nach Anspruch 1 oder 2, wobei die lichtemittierende Schicht aus einem PPV-Copolymer auf Acetatbasis gebildet wird.

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6. Verfahren nach Anspruch 6, wobei das Molverhältnis der Anodenschutzschicht 1:1,2 PEDT/PSS beträgt.

7. Verfahren nach Anspruch 6, wobei das Molverhältnis der Anodenschutzschicht 1:5 PEDT/PSS beträgt.

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8. Verfahren nach einem der vorhergehenden Ansprüche, wobei zwischen der Anodenschutzschicht und der lichtemittierenden Schicht eine weitere Schicht abgelagert wird, um die Beschichtungsgleichförmigkeit der lichtemittierenden Schicht zu verbessern.

9. Verfahren nach Anspruch 9, wobei die weitere Schicht Poly(vinylpyridin) (PVP) umfaßt.

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10. Verfahren nach einem der vorhergehenden Ansprüche, wobei zwischen der Anodenschutzschicht und der Kathode eine zweite lichtemittierende Schicht abgelagert wird.

11. Verfahren nach einem der Ansprüche 1 bis 5, wobei die Anodenschutzschicht bei Bildung aus Kohlenstoff, Zinnoxid oder Silizium durch Sputtern oder Aufdampfung gebildet wird.

55

12. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Dicke der Anodenschutzschicht zwischen 10 und 500 Å beträgt.

13. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Dicke der Anoden- und der lichtemittierenden

Schicht jeweils zwischen 500 und 2000 Å beträgt.

15. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Anode aus ITO gebildet wird.

5 16. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Kathode aus Aluminium oder einer Aluminiumlegierung gebildet wird.

17. Elektrolumineszenz-Bauelement, umfassend:

10 eine aus einem positive Ladungsträger injizierenden Material gebildete Anode;

eine auf der Anode aus einem Schutzmaterial gebildete Anodenschutzschicht, das aus der folgenden Gruppe ausgewählt wird: Polypyrrole und ihre Derivate;

15 Polyvinylcarbazol (PVK); Polystyrol; Poly(vinylpyridin); dielektrische Materialien; Kohlenstoff; amorphes Silizium; kein Indium enthaltende leitfähige Oxide, einschließlich Zinnoxid, Zinkoxid, Vanadiumoxid, Molybdänoxid und Nickeloxid;

20 eine aus einem halbleitenden konjugierten Polymer gebildete lichtemittierende Schicht; und

eine aus einem negative Ladungsträger injizierenden Material gebildete Kathode.

18. Bauelement nach Anspruch 17, wobei die Dicke der Anodenschutzschicht zwischen 10 und 500 Å beträgt.

25 19. Bauelement nach Anspruch 17 und 18, wobei die Dicke der Anoden- und der lichtemittierenden Schicht jeweils zwischen 500 und 2000 Å beträgt.

20. Bauelement nach einem der Ansprüche 17 bis 19, wobei die Anode aus ITO gebildet wird.

30 21. Bauelement nach einem der Ansprüche 17 bis 20, wobei die Kathode aus Aluminium oder einer Aluminiumlegierung gebildet wird.

22. Verfahren zur Herstellung eines Elektrolumineszenz-Bauelements, mit den folgenden Schritten:

35 Bilden einer Anode aus einem positive Ladungsträger injizierenden Material;

Bilden einer Opfer-Anodenschutzschicht über der Anode;

40 Ablagern eines Precursors für ein halbleitendes konjugiertes Polymer auf der Opferschicht;

Umwandeln des Precursors in ein halbleitendes konjugiertes Polymer, um eine lichtemittierende Schicht zu bilden, wobei während des Umwandlungsschritts die Anodenschutzschicht die Anode vor den Auswirkungen der Umwandlung schützt und selbst aufgebraucht wird; und

45 Bilden einer Kathode aus einem negative Ladungsträger injizierenden Material.

23. Verwendung einer Elektrodenschutzschicht bei der Herstellung eines organischen lichtemittierenden Bauelements, um eine Elektrode des organischen lichtemittierenden Bauelements vor den Auswirkungen der Umwandlung eines Precursors in ein lichtemittierendes halbleitendes konjugiertes Polymer zu schützen, wobei das organische lichtemittierende Bauelement eine erste und eine zweite Elektrode umfaßt und sich das lichtemittierende Polymer zwischen ihnen befindet.

24. Verwendung in einem Elektrolumineszenz-Bauelement, umfassend:

55 eine aus einem positive Ladungsträger injizierenden Material gebildete Anode, eine aus einem negative Ladungsträger injizierenden Material gebildete Kathode und eine aus einem halbleitenden konjugierten Polymer gebildete lichtemittierende Schicht, die sich zwischen der Anode und der Kathode befindet;

eine Schutzschicht zwischen der lichtemittierenden Schicht und der Anode, die aus einem aus der folgenden Gruppe ausgewählten Schutzmaterial gebildet wird: Polypyrrole und ihre Derivate; Polythiophene und ihre Derivate; Polyvinylcarbazol (PVK); Polystyrol; Poly(vinylpyridin); dielektrische Materialien; Kohlenstoff; amorphes Silizium; kein Indium enthaltende leitfähige Oxide, einschließlich Zinnoxid, Zinkoxid, Vanadiumoxid, Molybdänoxid und Nickeloxid zum Schutz der lichtemittierenden Schicht vor der Anode.

25. Verwendung nach Anspruch 24, wobei die Dicke der Schutzschicht zwischen 10 und 500 Å beträgt.

26. Verwendung nach Anspruch 24 oder 25, wobei die Dicke der Anoden- und der lichtemittierenden Schicht jeweils zwischen 500 und 2000 Å beträgt.

27. Verwendung nach Anspruch 24 und 26, wobei die Anode aus ITO gebildet wird.

28. Verwendung nach einem der Ansprüche 24 bis 27, wobei die Kathode aus Aluminium oder einer Aluminiumlegierung gebildet wird.

29. Elektrolumineszenz-Bauelement, umfassend:

eine aus einem positive Ladungsträger injizierenden Material gebildete Anode;

eine Schicht aus Polyethylenedioxythiophen-(PEDT-) polystyrolsulfonat (PSS) auf der Anode, wobei das Molverhältnis von PSS zu PEDT größer als 1,2:1 ist;

eine aus einem halbleitenden konjugierten Polymer gebildete lichtemittierende Schicht; und

eine aus einem negative Ladungsträger injizierenden Material gebildete Kathode.

30. Bauelement nach Anspruch 29, wobei das Molverhältnis von PSS zu PEDT 5:1 oder mehr beträgt.

Revendications

1. Procédé pour la production d'un dispositif électroluminescent, comprenant les étapes consistant :

à former une anode d'une matière d'injection de porteurs de charges positives ;
à former une couche de protection d'anode sur l'anode, constituée d'une matière protectrice choisie dans le groupe comprenant : des polypyrroles et leurs dérivés ; des polythiophènes et leurs dérivés ; le polyvinylcarbazole (PVK) ; le polystyrène ; la poly(vinylpyridine) ; des matériaux diélectriques ; le carbone ; le silicium amorphe ; des oxydes conducteurs ne contenant pas d'indium, comprenant l'oxyde d'étain, l'oxyde de zinc, l'oxyde de vanadium, l'oxyde de molybdène et l'oxyde de nickel ; et des semiconducteurs organiques sublimés ;
à former une couche électroluminescente en convertissant un précurseur en un polymère consistant en un polymère conjugué semiconducteur ; et
à former une cathode d'une matière d'injection de porteurs de charges négatives.

2. Procédé suivant la revendication 1, dans lequel le polymère conjugué semiconducteur est choisi dans une catégorie de polymères qui libèrent des sous-produits acides au cours de la conversion du polymère précurseur en le polymère conjugué.

3. Procédé suivant la revendication 1 ou 2, dans lequel l'anode comprend une couche conductrice transparente déposée sur un substrat constitué d'un verre ou d'une matière plastique.

4. Procédé suivant la revendication 1 ou 2, dans lequel la couche électroluminescente est formée d'un homopolymère de poly(p-phénylène-vinylène) (PPV).

5. Procédé suivant la revendication 1 ou 2, dans lequel la couche électroluminescente est formée d'un copolymère de PPV à base d'acétate.

6. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la couche protectrice d'anode est formée de polyéthylène-dioxythiophène/polystyrènesulfonate.
- 5 7. Procédé suivant la revendication 6, dans lequel le rapport molaire PEDT/PSS de la couche protectrice d'anode est égal à 1:1,2.
8. Procédé suivant la revendication 6, dans lequel le rapport molaire PEDT/PSS de la couche protectrice d'anode est égal à 1:5.
- 10 9. Procédé suivant l'une quelconque des revendications précédentes, dans lequel une couche supplémentaire est déposée entre la couche protectrice d'anode et la couche électroluminescente pour améliorer l'uniformité du revêtement de la couche électroluminescente.
- 15 10. Procédé suivant la revendication 9, dans lequel la couche supplémentaire comprend de la poly(vinylpyridine) (PVP).
11. Procédé suivant l'une quelconque des revendications précédentes, dans lequel une seconde couche électroluminescente est présente entre la couche protectrice d'anode et la cathode.
- 20 12. Procédé suivant l'une quelconque des revendications 1 à 5, dans lequel, lorsque la couche protectrice d'anode est formée de carbone, d'oxyde d'étain ou de silicium, elle est formée par pulvérisation cathodique ou évaporation.
13. Procédé suivant l'une quelconque des revendications précédentes, dans lequel l'épaisseur de la couche protectrice d'anode est comprise dans l'intervalle de 10 à 500 Å.
- 25 14. Procédé suivant l'une quelconque des revendications précédentes, dans lequel l'épaisseur de chacun des éléments consistant en l'anode et la couche électroluminescente est comprise dans l'intervalle de 500 à 2000 Å.
15. Procédé suivant l'une quelconque des revendications précédentes, dans lequel l'anode est formée de ITO.
- 30 16. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la cathode est formée d'aluminium ou d'un alliage d'aluminium.
- 35 17. Dispositif électroluminescent comprenant :
 - une anode formée d'une matière d'injection de porteurs de charges positives ;
 - une couche protectrice d'anode sur la cathode, formée d'une matière protectrice choisie dans le groupe comprenant : des polypyrroles et leurs dérivés ; le polyvinylcarbazole (PVK) ; le polystyrène ; la poly(vinylpyridine) ; des matériaux diélectriques ; le carbone ; le silicium amorphe ; des oxydes conducteurs ne contenant pas d'indium, comprenant l'oxyde d'étain, l'oxyde de zinc, l'oxyde de vanadium, l'oxyde de molybdène et l'oxyde de nickel ;
 - une couche électroluminescente formée d'un polymère conjugué semiconducteur ; et
 - une cathode formée d'une matière d'injection de porteurs de charges négatives.
- 45 18. Dispositif suivant la revendication 17, dans lequel l'épaisseur de la couche protectrice d'anode est comprise dans l'intervalle de 10 à 500 Å.
19. Dispositif suivant la revendication 17 ou 18, dans lequel l'épaisseur de chacun des éléments consistant en l'anode et la couche électroluminescente est comprise dans l'intervalle de 500 à 2000 Å.
- 50 20. Dispositif suivant l'une quelconque des revendications 17 à 19, dans lequel l'anode est formée de ITO.
21. Dispositif suivant l'une quelconque des revendications 17 à 20, dans lequel la cathode est formée d'aluminium ou d'un alliage d'aluminium.
- 55 22. Procédé pour la production d'un dispositif électroluminescent, comprenant les étapes consistant :
 - à former une anode d'une matière d'injection de charges positives ;

à former une couche sacrificielle protectrice d'anode sur l'anode ;
à déposer un précurseur d'un polymère conjugué semiconducteur sur la couche sacrificielle ;
à convertir le précurseur en un polymère conjugué semiconducteur pour former une couche électroluminescente, étape de conversion pendant laquelle la couche protectrice d'anode protège l'anode contre les effets de la conversion et est elle-même consommée ; et
à former une cathode d'une matière d'injection de charges négatives.

23. Utilisation d'une couche protectrice d'électrode dans la production d'un dispositif organique électroluminescent pour protéger une électrode du dispositif organique électroluminescent contre les effets de la conversion d'un précurseur en un polymère conjugué semiconducteur électroluminescent, dans laquelle le dispositif organique électroluminescent comprend des première et seconde électrodes, avec le polymère électroluminescent présent entre ces électrodes.

24. Utilisation dans un dispositif électroluminescent comprenant :

une anode formée d'une matière d'injection de porteurs de charges positives, une cathode formée d'une matière d'injection de porteurs de charges négatives et une couche électroluminescente formée d'un polymère conjugué semiconducteur situé entre l'anode et la cathode ;
d'une couche protectrice située entre la couche électroluminescente et l'anode et formée d'une matière protectrice choisie dans le groupe comprenant : des polypyrroles et leurs dérivés ; des polythiophènes et leurs dérivés ; le polyvinylcarbazole (PVK) ; le polystyrène ; la poly(vinylpyridine) ; des matériaux diélectriques ; le carbone ; le silicium amorphe ; des oxydes conducteurs ne contenant pas d'indium, comprenant l'oxyde d'étain, l'oxyde de zinc, l'oxyde de vanadium, l'oxyde de molybdène et l'oxyde de nickel, pour protéger la couche électroluminescente contre l'anode.

25. Utilisation suivant la revendication 24, dans laquelle l'épaisseur de la couche protectrice est comprise dans l'intervalle de 10 à 500 Å.

26. Utilisation suivant la revendication 24 ou 25, dans laquelle l'épaisseur de chacun des éléments consistant en l'anode et la couche électroluminescente est comprise dans l'intervalle de 500 à 2000 Å.

27. Utilisation suivant l'une quelconque des revendications 24 à 26, dans laquelle l'anode est formée de ITO.

28. Utilisation suivant l'une quelconque des revendications 24 à 27, dans laquelle la cathode est formée d'aluminium ou d'un alliage d'aluminium.

29. Dispositif électroluminescent comprenant :

une anode formée d'une matière d'injection de porteurs de charges positives ;
une couche de polyéthylène-dioxythiophène (PEDT)/polystyrènesulfonate (PSS) sur l'anode, le rapport molaire du PSS au PEDT étant supérieur à 1,2:1 ;
une couche électroluminescente formée d'un polymère conjugué semiconducteur ; et
une cathode formée d'une matière d'injection de porteurs de charges négatives.

30. Dispositif suivant la revendication 29, dans lequel le rapport molaire du PSS au PEDT est égal ou supérieur à 5:1.

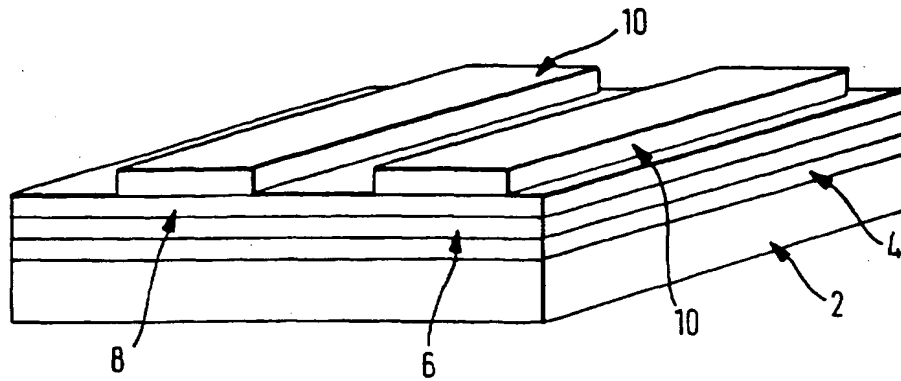


FIG. 1A

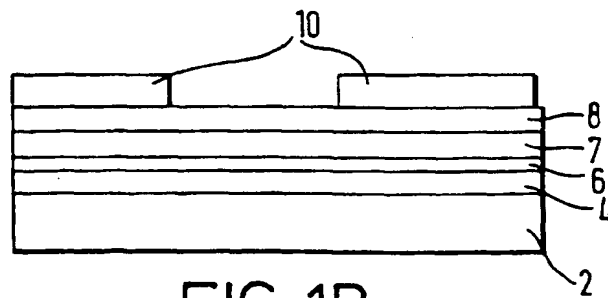


FIG. 1B

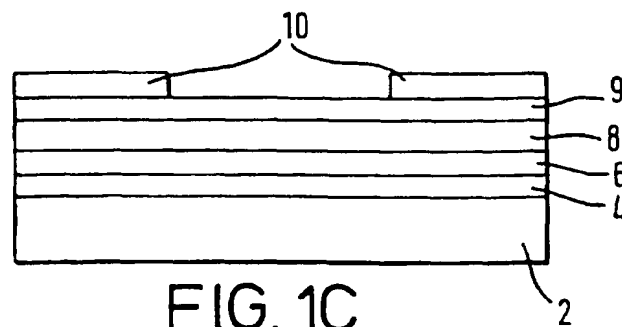


FIG. 1C

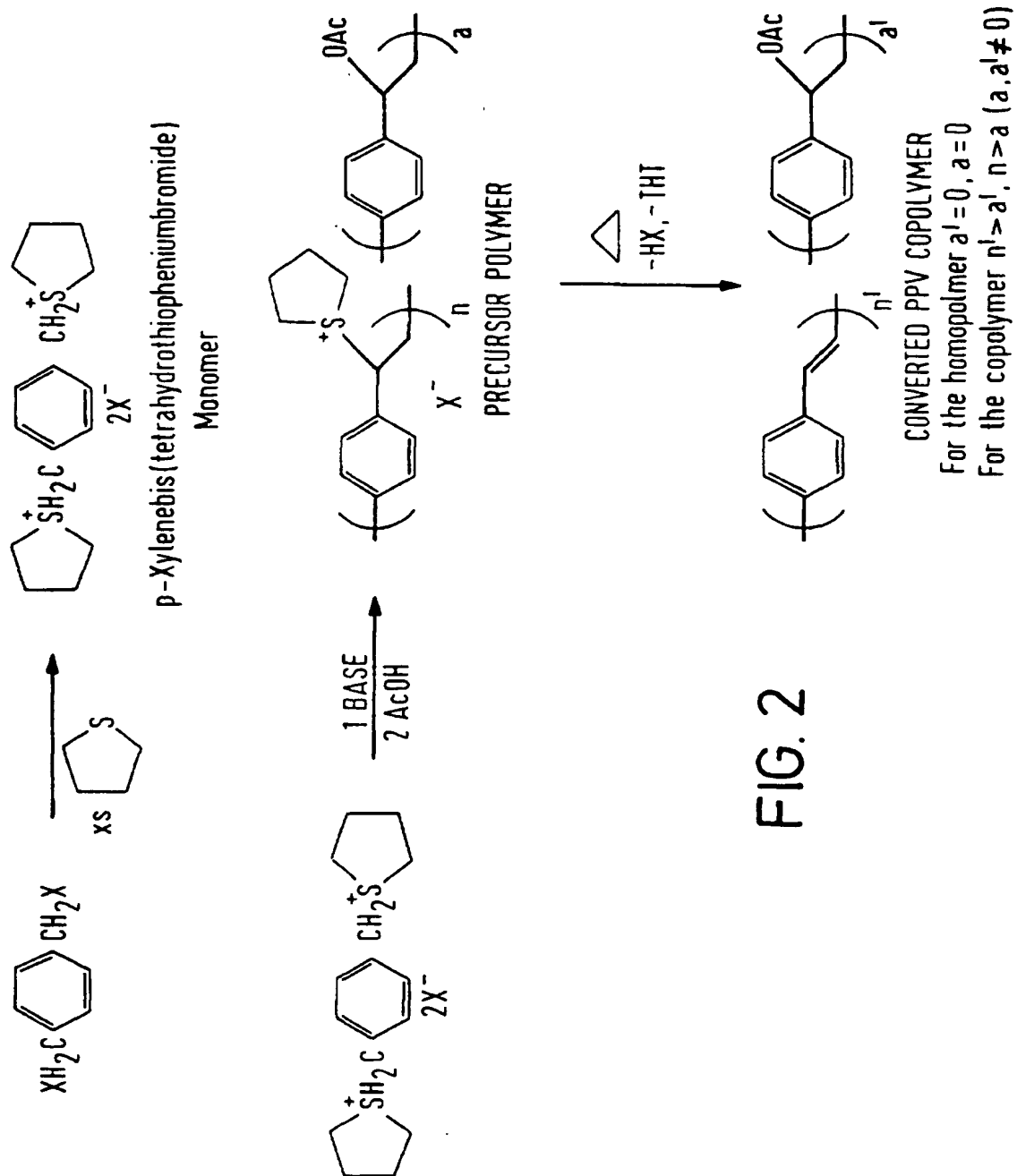


FIG. 2

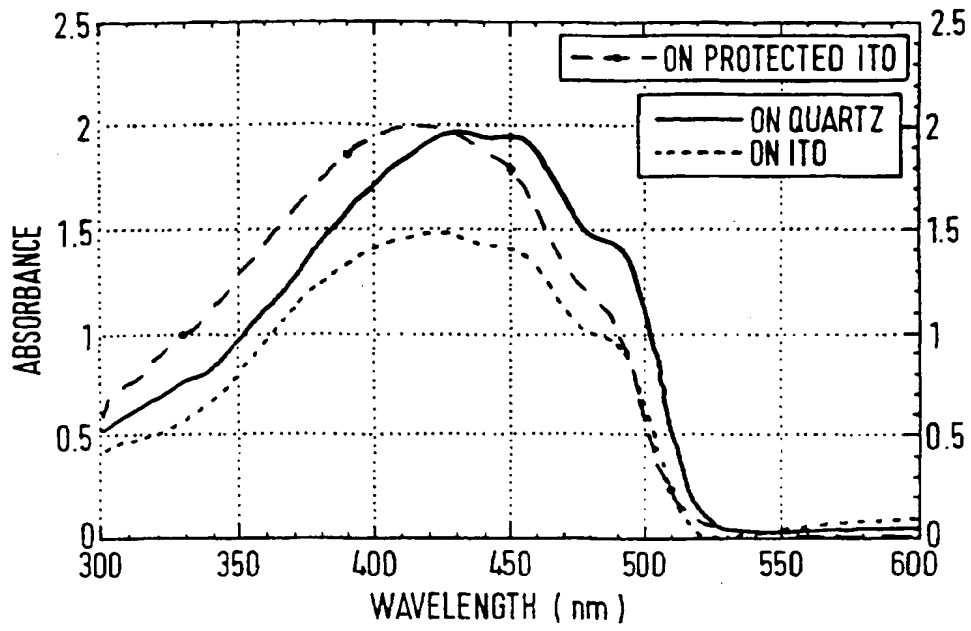


FIG. 3A

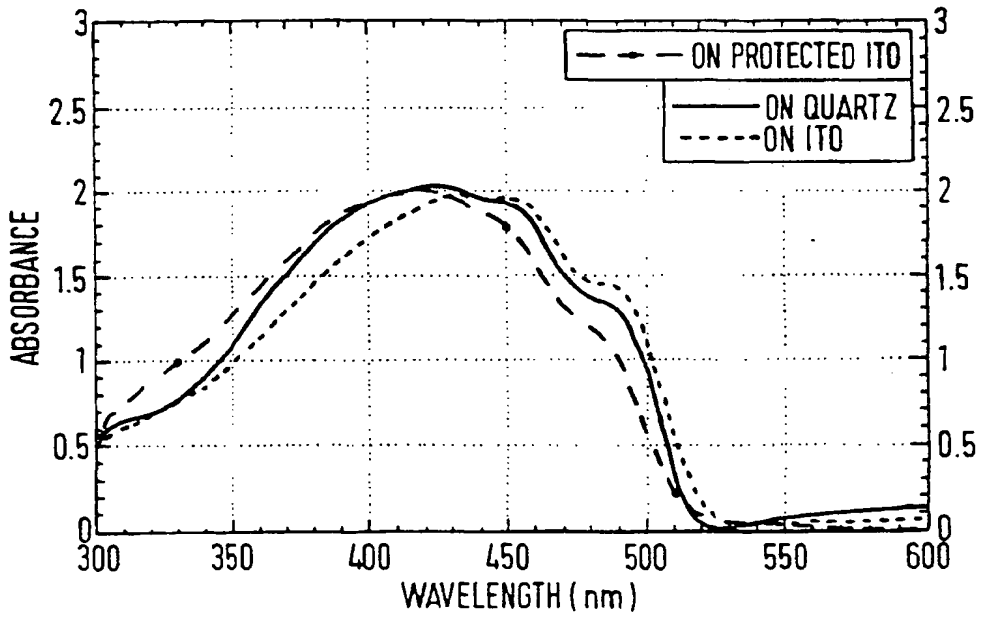


FIG. 3B

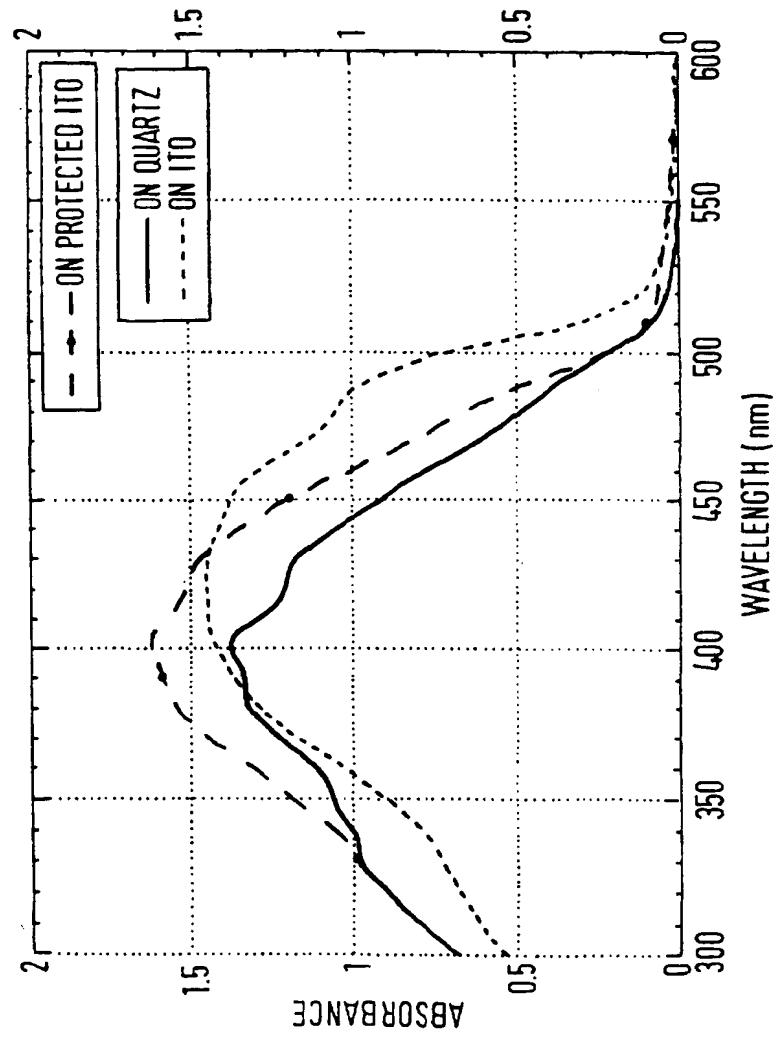


FIG. 4

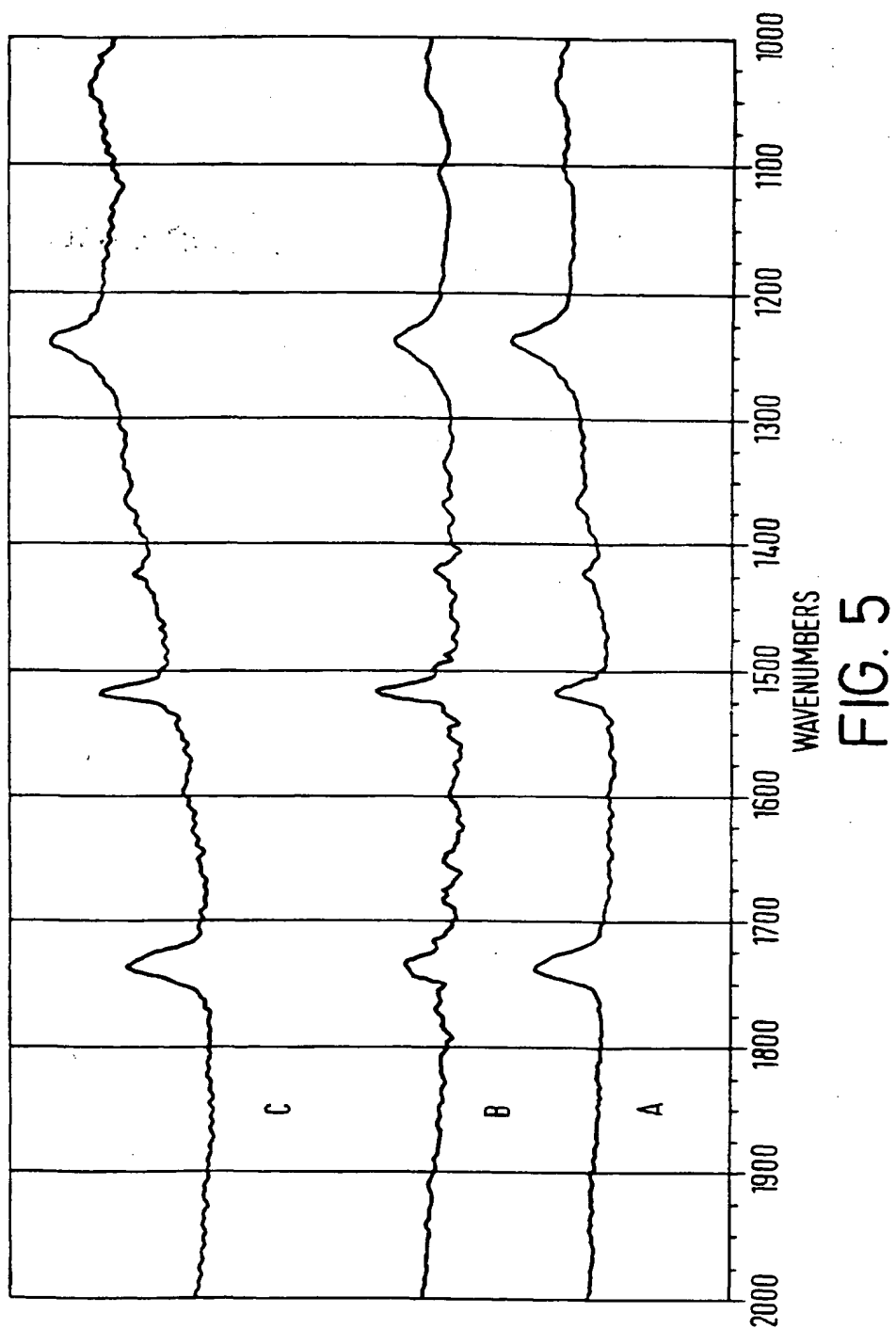


FIG. 5

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